EFFECTS OF DIFFERENT ELECTRO CHEMICAL CELLS, PARTICLE SIZE AND LOCAL PH ON CO_2 REDUCTION REACTION

by

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Abstract

In effort to mitigate global warming, electrochemical reduction of carbon dioxide is extensively studied as a promising technique to decrease the atmospheric carbon dioxide level. This technique recycles gaseous carbon dioxide into reusable form of energy by applying electrical energy while allowing the gas to react with a catalyst. Many types of metallic nano-catalyst, ranging from gold, copper, platinum and etc., have been shown in researches to successfully regenerate fuels such as carbon monoxide, hydrocarbons.

There have been many scientific efforts to optimize the condition in which electrochemical reduction yields more of the wanted product energy form, and less of unwanted products, or byproducts. The focus is not only in higher yields of reusable energy but also in efficiency in yielding the results.

Gold nanoparticles in electrochemical reduction of CO_2 is studied quite abundantly, and known as a fact that the reaction will produce carbon monoxide (CO) for the most of the time in reasonable overpotentials. From electrochemical reduction of water, hydrogen evolves. So, we took the advantage of this characteristic of gold nanoparticles, and choose to conduct our study on gold.

Many factors affect the efficiency of the electrochemical reduction reaction. Considering many factors, diffusivity was one major factor that could affect the reaction. Traditionally, scientist worked on H-cell for electrochemical reduction project. It had catalyst immersed in aqueous solutions to help ion transfer. However, the limitation was in the diffusivity of CO_2. The diffusivity of CO_2 is Water (H_2O) is around 2.3×10^{-9} m^2/s, where as the diffusivity in air is 1.4×10^{-5} m^2/s. The diffusivity is almost 5000 larger in air. So we came up with a design to create an interface where CO_2 can migrate to the catalyst surface via gas

phase but keep protons and other constituents migrate via liquid phase, namely, gas diffusion electrolyzer (GDE).

Another factor that may affect the efficiency is the local pH during the reaction. Since gold nanoparticles generate H_2 gas during it's the reduction from hydrogen evolution reaction (HER), the local pH tends to increase during the experiment. So, we hypnotized that if the local pH increased would lead to suppression of HER, and thus follow up with a increased selectivity for CO.

We hypothesize that increase in gas diffusivity into the catalyst, catalytic surface area, and local pH will positively affect the electrochemical reduction of carbon dioxide. My work looks into the aspects of the nature of the electrochemical cell by comparing two cell types that differ in carbon dioxide diffusivity, by comparing different catalyst sizes of gold nanoparticles that differ in surface to volume ratio, and local pH in which the reaction takes place. Through this work, we will get an insight of how to develop efficient electrochemical reduction conditions.

Advisor: Dr. Chao Wang

Reader: Dr. Chao Wang

Table of Contents

1. Introduction

One of the biggest problems the world is facing is global warming. Increased consumption of fossil fuels from industrial revolution has led to increased carbon dioxide gas emission. Carbon dioxide as we know is one of the major green house gasses that causes climate change. According to NASA climate, atmospheric carbon dioxide levels has increased from 280 ppm to 400 ppm in the last 150 years, mainly from the industrial activities [1]. In efforts to reduce the rate of the climate change, scientists are looking for clean and renewable energy sources that environmentally friendly. Natural energy sources such as solar energy and wind energy has been considered as a next generation energy source, but they lacked stability due to nature conditions while taking up large landmass for their installation.

Scientists has moved their focus from natural energy sources to renewable carbon-based energy sources. One of the promising technologies in achieving renewable carbon-based energy is electrochemical reduction. Electrochemical reduction of carbon source, usually carbon dioxide, a byproduct in the use of energy, is consumed to form usable hydrocarbon products. Electrochemical reduction process does not highly depend on thermodynamics but rather depend on the kinetics. The focus of the process lies on generating as much desired product, which is selectivity, and less unwanted byproducts at low electrochemical potential.

Monodispersed gold nanoparticles particularly produce carbon monoxide in electrochemical reduction process. Its single product reaction gives much clear and insight on factors that affect the efficiency and selectivity of the process. In this report, we will discuss the effects of different mass transfer method through different electrochemical cell design, different particle size, and different local pH.

2. Experimental

2.1 Chemical and Materials

Tetrachloroauric (III) acid trihydrate (HAuCl4 · 3H2O, 99%) was used as received.

2.2 Preparation of gold nanoparticles

2.2.1 Monodisperse gold nanoparticle synthesis

In synthesizing gold nanoparticles, we followed an as-synthesis method [2]. Solution of Tetrachloroauric (III) acid trihydrate, Toluene, Oleylamine were stirred in room temperature for 10 minute under constant feed of Nitrogen Gas. Then, Borane tert-butylamine, Oleyamine solution is injected and stirred for 1 hour to form 5 nm gold particles.

2 nm gold particles were synthesized in similar matter, but 40 degrees Celsius in both stirring stages.

2.2.1 Loading nanoparticles on Carbon

Synthesized gold nanoparticles were loaded on Tanaka Carbon, by sonicating the synthesized nanoparticles for 30 minutes in toluene, ethanol mixture with carbon added. Then the nanoparticles on carbon are dried then annealed at 185 degrees Celsius.

2.3 Characterization techniques

Scanning electron microscopy (SEM, JEOL JSM-6700F) and energy dispersive X-ray spectroscopy (EDS) were used to characterize the size and shape and the surface composition of the sample. Inductively coupled plasma mass spectrometry (ICP-MS) was done to samples after each experiment for accurate loading of the catalyst.

2.4 Electrochemical Measurements

Electrochemical reduction reaction was measured on Autolab Nova setup with 2 different cell types, different pH solutions. Anion exchange membrane was used, and chemical potential range of -200 mV to -800 mV, versus RHE, were measured for each 100 mV intervals. Hg/HgO electrode was used as reference electrode.

$$E_{RHE} = E_{Hg/HgO} + 0.140\ V + 0.059\ (pH)$$

2.4.1 H-cell

Traditional H-cell experiment were done on 5 nm gold catalyst, with 0.5 M $KHCO_3$ solution with pH of 8.9, 20 ug of catalyst were used. 10 mL sample volume was used each batch of potential intervals, while constant purge of 20 sccm CO_2.

2.4.2 GDE

On same loading of catalyst and same solution, a liquid solution flow of 0.5 mL/min was let flow through the cell, and 8 sccm of CO_2 flow.

Both 20 sccm gas flow in H-cell and 8 sccm gas flow in GDE were considered to provide sufficient CO_2 in the experiments, from approximate calculations based on the mass transfer of CO_2.

3. Results and Discussion

3.1 Synthesis of gold nanoparticles

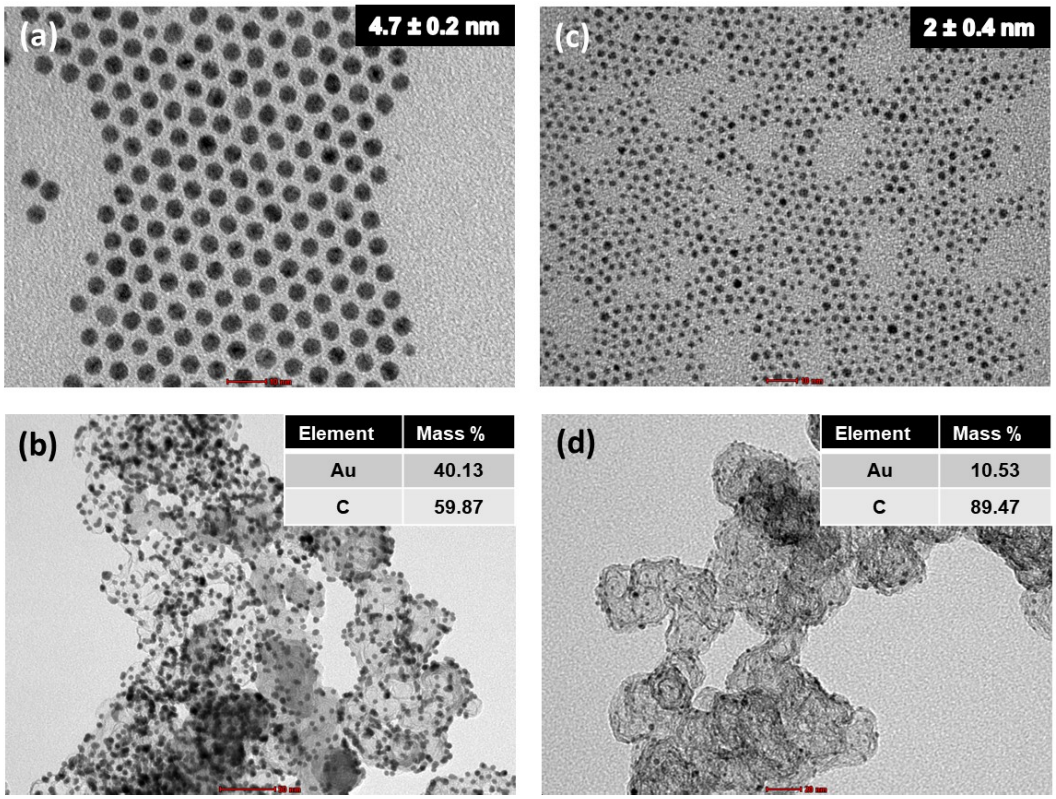

Figure 1. Electron microscopy images of: (a) 5 nm gold nanoparticles, (b) 5 nm gold nanoparticles loaded on carbon and its composition, (c) 2 nm gold nanoparticles, and (d) 2 nm gold particles loaded on carbon and its composition

As shown in Figure 1, 5 nm gold catalyst were ~40 wt% gold particles, and ~11 wt% for 2 nm gold catalyst. The compositions were accurately put into considerations in further calculations for comparison.

3.2 H-cell versus GDE

From the two different electro-chemical cell set-ups, the following data was acquired.

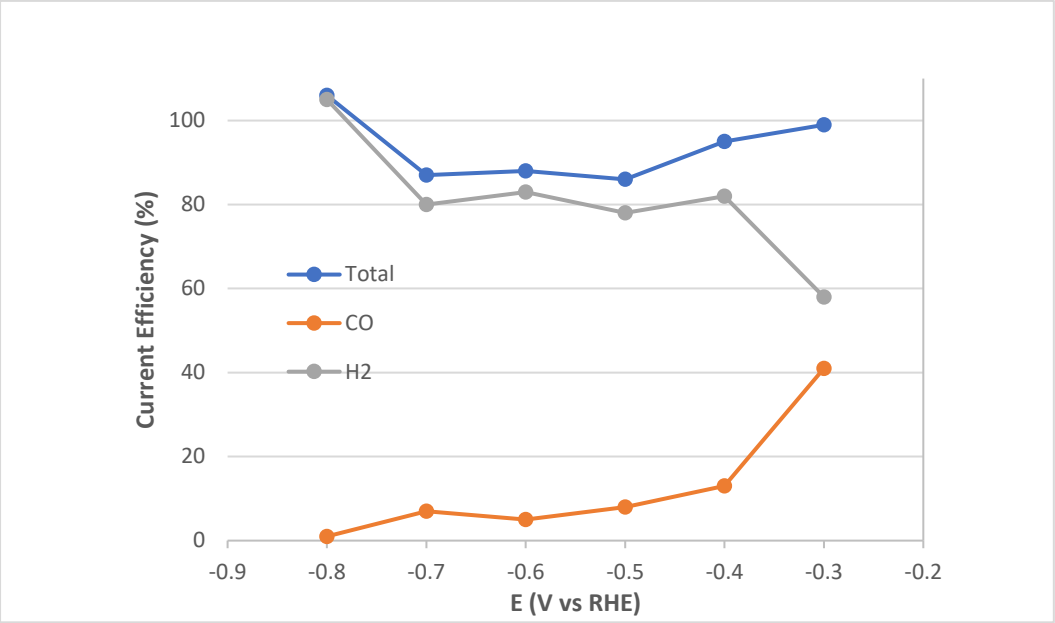

Figure 2. Current efficiency from H-cell.

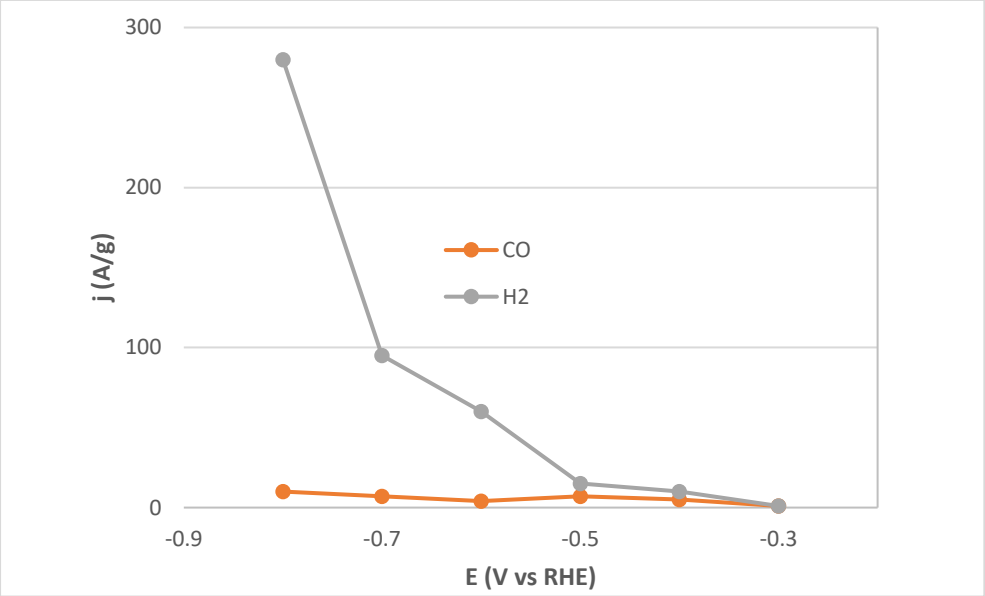

Figure 3. Mass activity of the catalyst for products.

It is evident that CO selectivity decreases for higher overpotentials, as HER reaction overtakes the process.

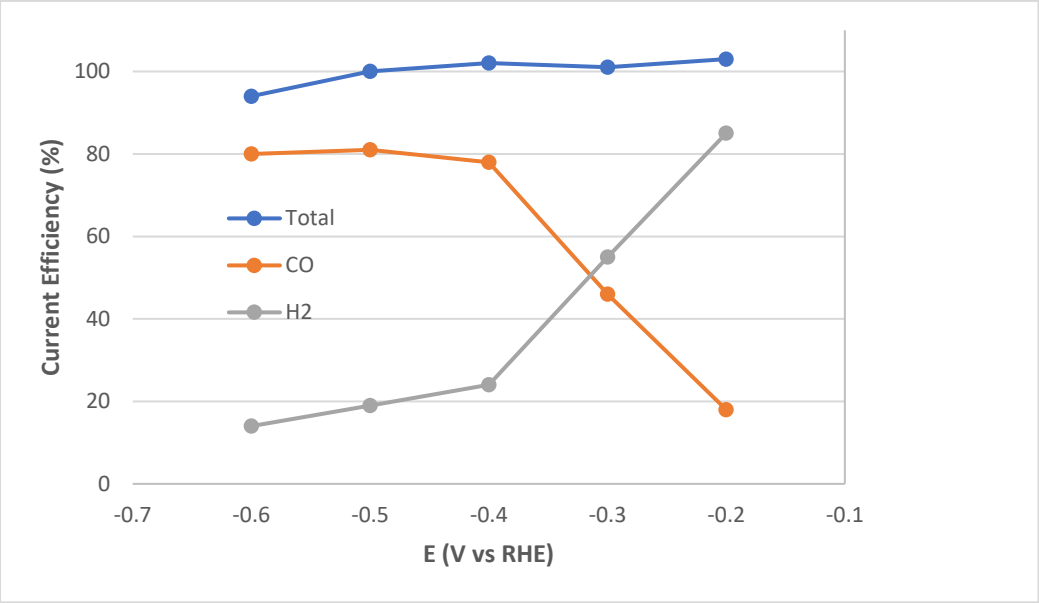

Figure 4. Current efficiency from 5 nm gold nanoparticles in 0.5M $KHCO_3$ in GDE set-up.

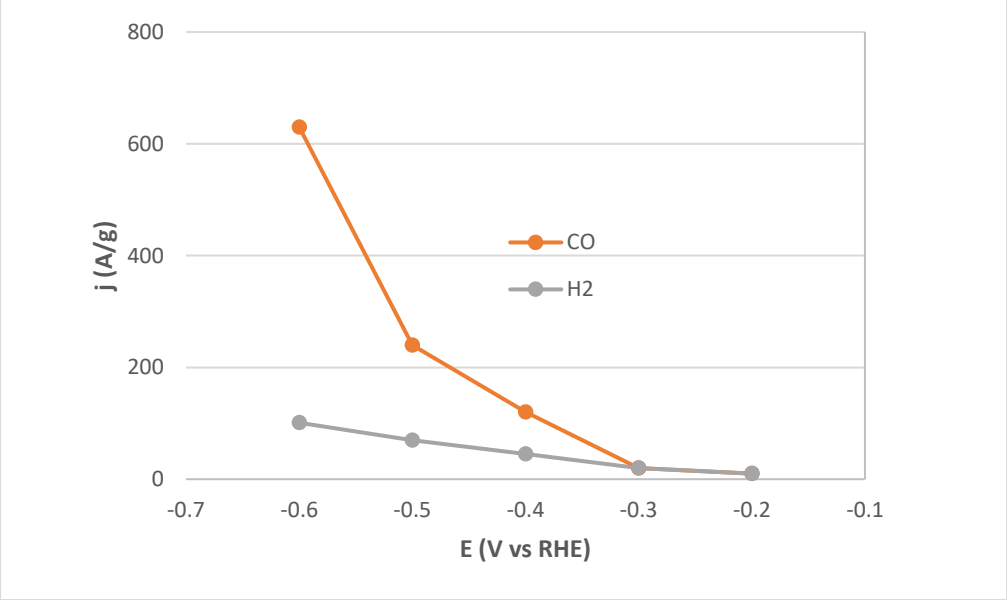

Figure 5. Mass activity in GDE from 5nm gold nanoparticles in 0.5M $KHCO_3$.

The trend for current efficiency and mass activity is significantly different between H-cell and GDE.

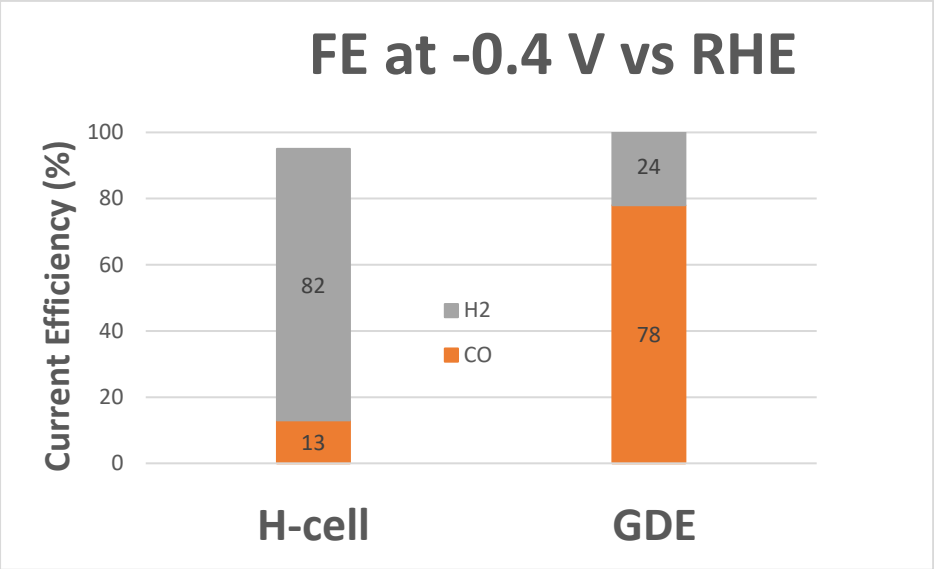

Figure 6. Current Efficiency for two different set-up at -0.4 V versus RHE.

From figure 4, there is a cross over of CO selectivity in GDE, which is a different trend compared to H-cell. Figure 6 shows how when preparing the catalyst and support material the exact same way the performance is drastically different in the two electrochemical cells, where H-cell is delivering CO_2 to the electrode via liquid phase and GDE via gaseous phase.

3.3 Different Particle size on GDE set-up

Electrochemical reduction reaction of CO_2 was performed on both catalysts, sized of 2 nm and 5 nm. Based on the previous experiment of H-cell versus GDE, the experiments were performed in GDE set-up.

Following figures (Figure 7 and 8) shows a similar trend in current efficiency of each elements, but changes in different overpotentials.

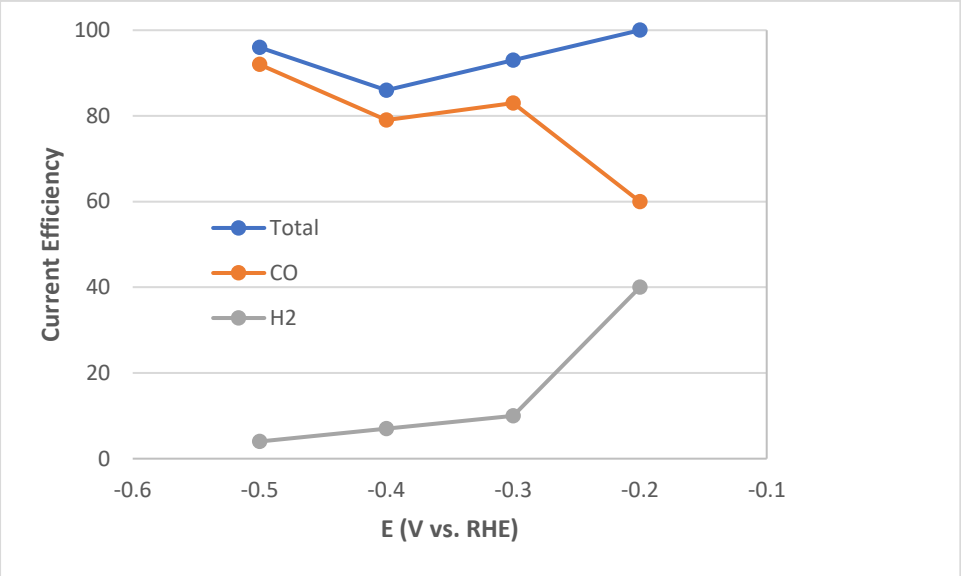

Figure 7. Current Efficiency for 2 nm gold particles

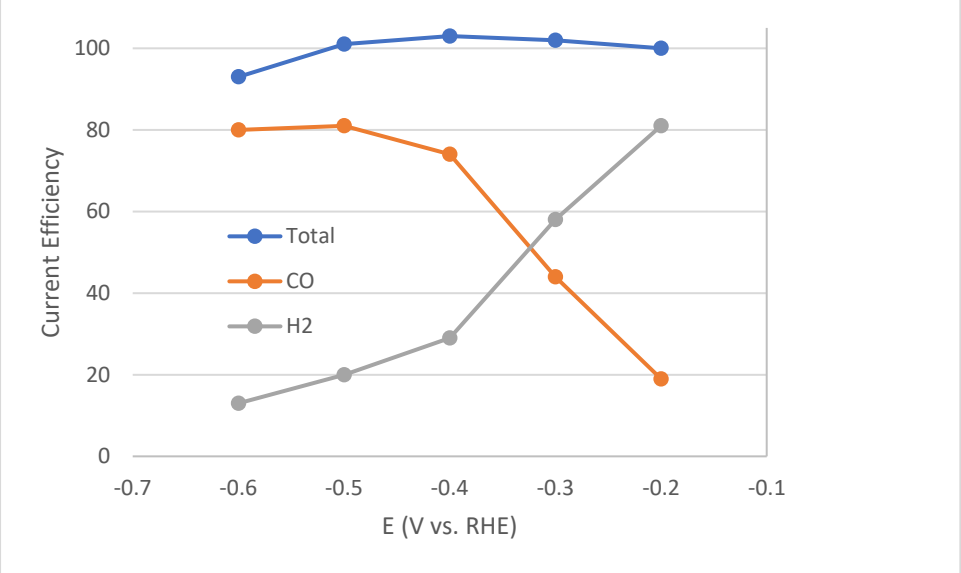

Figure 8. Current efficiency for 5 nm gold particles

To easily compare the two, an extra figure of direct comparison of the who particle size catalyst at -0.3V versus RHE was generated.

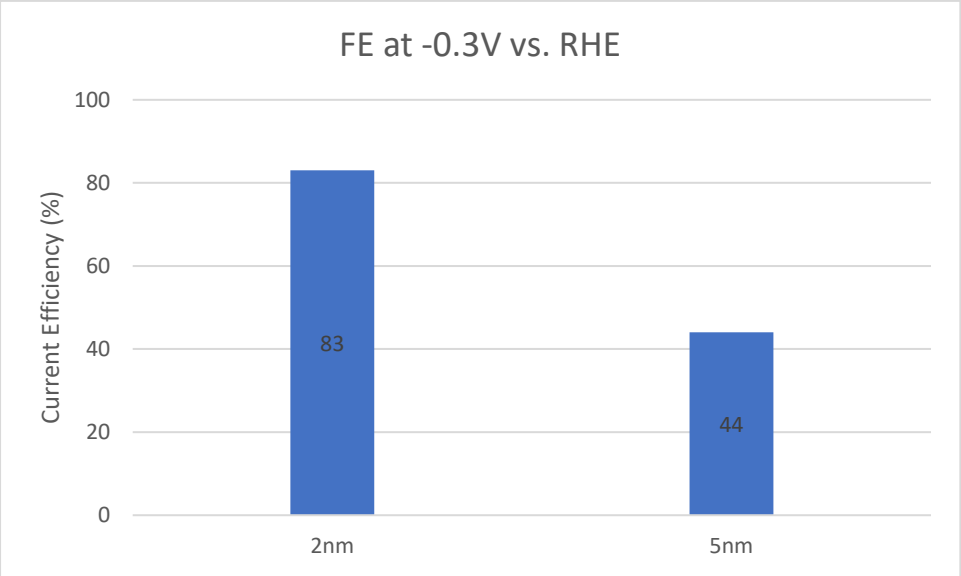

Figure 9. Comparison of current efficiency at -0.3 V vs. RHE

The trends in figures 7,8,9 show lower CO onset potential for 2 nm particles.

3.4 Local pH effects

For comparing local pH affects on the reduction reaction, we decide to look into the result in two methods. One being the standardized potential in Reverse Hydrogen Electrode (RHE) and Standardized Hydrogen Electrode (SHE) being the other.

3.4.1 Comparison in RHE

Comparing different local pH effect in RHE, the selectivity is high for high pH at low potentials. Specific activity if higher in higher pH.

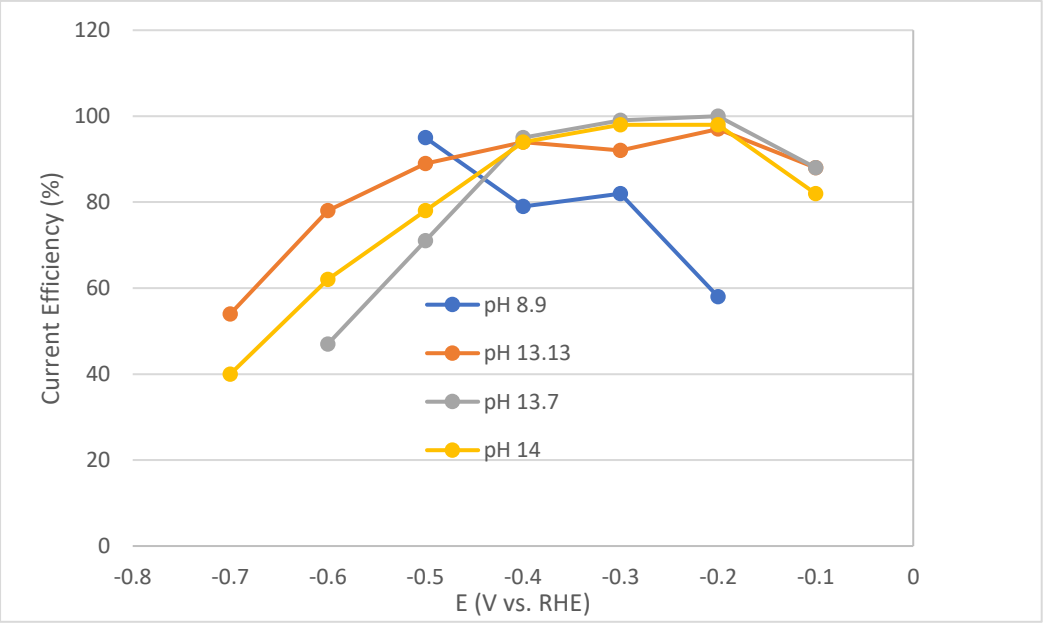

Figure 10. Current efficiency of CO in different pH in RHE scale

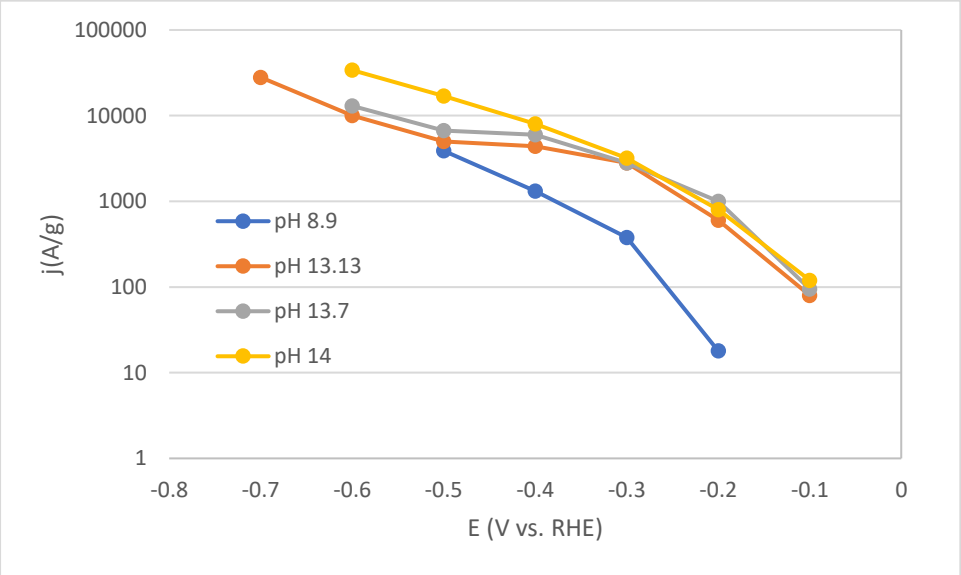

Figure 11. Mass selectivity of CO in different pH in RHE scale

3.4.2 Comparison in SHE

Comparing the local pH in SHE standards, mass activity is similar in trend, and somewhat overlapping.

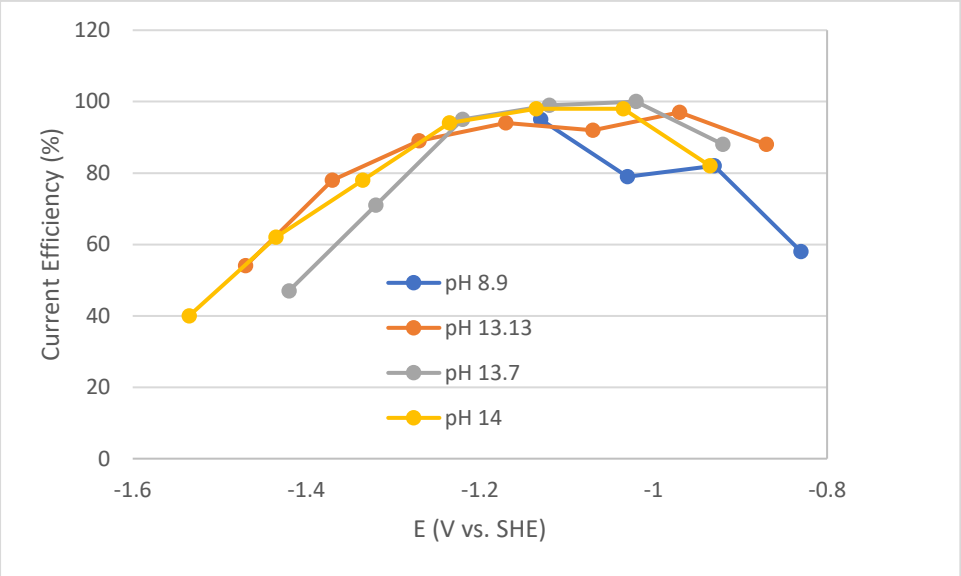

Figure 12. Current efficiency of CO in different pH in SHE scale

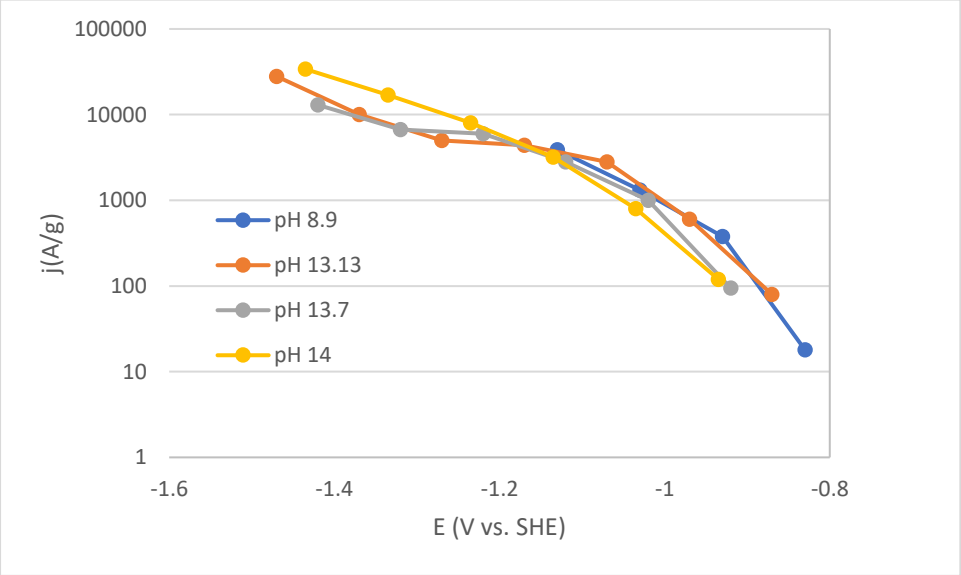

Figure 13. Mass selectivity of CO in different pH in SHE scale

The selectivity increases at lower overpotentials up to -0.4 V versus RHE, but decreases at higher overpotentials as pH increases.

4. Conclusion

In this report, we conclude on few important factors that affect the selectivity and efficiency of electrochemical reduction reaction. The diffusivity of CO_2 gas has significant role in the reaction. GDE significantly enhances the selectivity of CO_2 reduction, compared to H-cell. There may have been diffusivity limitation issues in previous research in H-cell set-up, depending on the design of the experiment.

The particle size of the catalyst plays a role in selectivity. In this report, the selectivity difference in not as big, but 2 nm gold particles seemed to have a slightly higher specific activity. Most importantly, the effects of local pH on CO_2 reaction is surprising. We conclude that more alkaline conditions well reduce the HER reaction, and does push towards CO production. The onset potential of CO decreases as pH increases, and higher pH increases the mass activity of CO. The selectivity is higher at lower overpotentials, but decreases sooner at higher overpotentials.

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2. A Facile Synthesis of Monodisperse Au Nanoparticles and Their Catalysis of CO Oxidation
   Sheng Peng1 , Youngmin Lee1 , Chao Wang1 , Hongfeng Yin2 , Sheng Dai2 , and Shouheng Sun1

Curriculum Vitae

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Education

- **Johns Hopkins University** **Baltimore, MD**
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Publications

- "Thermal Oxidation-Driven Growth of Hierarchical Copper Nanofoams as Advanced CO2 Electrocatalysts." Raciti, D.; Wang, B; Mao, M.; Park, J. H.; Wang, C. *in preparation*
- "Mass Transfer Effects in CO2 Reduction on Cu Nonowire Electrocatalysts." Raciti, D.; Mao, M.; Park, J.H.; Wang, C.
- "Three-Dimensional Hierarchical Copper-Based Nanostructures as Advanced Electrocatalysts for CO2 Reduction." Raciti, D.; Wang, Y.; Park, J.H.; Wang, C.
- "Local pH Effect in the CO2 Reduction Reaction on High-Surface-Area Copper Electrocatalysts." Raciti, D.; Mao, M.; Park, J.H.; Wang, C
- "Electro-Oxidation of Ethanol Using Pt3Sn Alloy Nanoparticles." Liu, Y.; Wei, M.; Raciti, D.; Hu, P.; Park, J.H.; Barclay, M.; Wang, C

Professional Experience

- **Nano Energy Laboratory** **Baltimore, MD**

  September 2016 – Present
  - Synthesis of metallic nano catalyst for use in CO_2 reduction, Alcohol oxidation for clean energy generation

Skills and Language

- **Lab Skills & Instruments** – Nanoparticle synthesis, Electrochemical Experiments using AutoLab, Gas Chromatography using GCMS, TEM/SEM, NMR
- **Computer** – MATLAB, Python, Origin
- **Language** – Fluent in Korean and English

Extracurricular

- **ROK Army, 61st Infantry Division Headquarters** **Incheon, South Korea**

  Division Commander's(Brigadier General) Secretarial Driver November, 2013 - April, 2015
  - Position for soldiers with great mentality, physical ability, and work ethic
  - Worked as secretary, organizing General's daily schedule with precision

  Squad leader, a squad of drivers October, 2014 – March, 2015
  - Lead squad missions. Took care of squadrons physically, and mentally, and gave help whenever needed. Learned what good leader types are and the leader type that fit me the most